

6.11

The mean separation, \bar{x} , is found from the probability that the separation is between x and $x+dx$.

$$P(x)dx \propto e^{-\frac{U(x)}{kT}} dx \quad \text{where } U(x) = U_0 \left[\left(\frac{a}{x}\right)^2 - 2\left(\frac{a}{x}\right)^6 \right]$$

It's easily verified that the minimum of the potential is at $x=a$. Since departures from this position are small, we may expand $U(x)$ about a to obtain

$$U(x) \approx -U_0 + \frac{36U_0}{a^2}(x-a)^2 - \frac{252U_0}{a^3}(x-a)^3$$

where we have kept only the first three terms. It follows that

$$P(x)dx = C \exp \left[-\frac{36U_0(x-a)^2}{a^2 kT} + \frac{252U_0(x-a)^3}{a^3 kT} \right] dx$$

We have absorbed the irrelevant constant term, $e^{-\frac{U_0}{kT}}$, into the normalization constant C . This constant is evaluated from the usual requirement

$$\int_{-\infty}^{\infty} P(x)dx = C \int_{-\infty}^{\infty} \exp \left[-\frac{36U_0(x-a)^2}{a^2 kT} \right] \exp \left[\frac{252U_0(x-a)^3}{a^3 kT} \right] dx = 1$$

The predominant factor in the integrand is $\exp \left[-\frac{36U_0(x-a)^2}{a^2 kT} \right]$ so the second factor may be expanded in a Taylor's series as in Appendix A.6. Furthermore, the region of integration can be extended to $-\infty$ since the exponential is negligibly small except near a .

$$\text{Thus } I = C \int_{-\infty}^{\infty} \exp \left[-\frac{36U_0(x-a)^2}{a^2 kT} \right] \left(1 + \frac{252U_0(x-a)^3}{a^3 kT} \right) dx \quad (1)$$

where we neglect all but the first two terms. The first integral is evaluated in Appendix A.4 while the second is 0 since the integrand is an odd function.

$$\text{Then } C = \frac{6}{a} \left(\frac{U_0}{\pi kT} \right)^{\frac{1}{2}}$$

By definition, $\bar{x} = \int_{-\infty}^{\infty} x P(x)dx$, and to the same approximation as in (1) we have

$$\bar{x} = \int_{-\infty}^{\infty} x \left(\frac{6}{a} \right) \left(\frac{U_0}{\pi kT} \right)^{\frac{1}{2}} \exp \left[-\frac{36U_0(x-a)^2}{a^2 kT} \right] \left(1 + \frac{252U_0(x-a)^3}{a^3 kT} \right) dx$$

The first term in the integrand is a Gaussian times x and the integral is just a . The second may be evaluated by making the substitution $\xi = x-a$

$$\bar{x} = a + \frac{6}{a} \left(\frac{U_0}{\pi kT} \right)^{\frac{1}{2}} \frac{252U_0}{a^3 kT} \left[\int_{-\infty}^{\infty} \xi^4 \exp \left[-\left(\frac{36U_0}{a^2 kT} \right) \xi^2 \right] d\xi + \int_{-\infty}^{\infty} a \xi^3 \exp \left[-\left(\frac{36U_0}{a^2 kT} \right) \xi^2 \right] d\xi \right]$$

Noting that the second integral is 0 since the integrand is an odd function, and evaluating the first by Appendix A.4, we find $\bar{x} = a \left(1 + \frac{0.15 kT}{U_0} \right)$

$$\text{Thus } \alpha = \frac{1}{\bar{x}} \frac{d\bar{x}}{dT} = \frac{0.15 k}{a U_0 + (0.15) a k T} \approx \frac{0.15 k}{U_0} \quad \text{since } U_0 \gg kT$$

7.1

(a) We label the positions and momenta such that r_{ij} and p_{ij} refer to the j^{th} molecule of type i . There are N_i molecules of species i . Then the classical partition function for the mixture of ideal gases is

$$Z' = \int \exp \left[-\frac{\beta}{2m_1} (\underline{p}_{11}^2 + \dots + \underline{p}_{1N_1}^2) - \dots - \frac{\beta}{2m_K} (\underline{p}_{K1}^2 + \dots + \underline{p}_{KN_K}^2) \right] \frac{d^3r_{11} \dots d^3r_{KN_K} d^3p_{11} \dots d^3p_{KN_K}}{h_0^{3N_1} \dots h_0^{3N_K}}$$

The integrations over r yield the volume, V , while the p integrals are identical. Since there are $N_1 + N_2 + \dots + N_K$ integrations, we have

$$Z' = V^{(N_1 + \dots + N_K)} \left[\int e^{-\frac{\beta p^2}{2m}} \frac{d^3p}{h_0^3} \right]^{(N_1 + \dots + N_K)}$$

The term in brackets is independent of volume, consequently

$$\ln Z' = (N_1 + \dots + N_K) \ln V + \ln(\text{constant})$$

$$\text{and } \bar{p} = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z' = (N_1 + \dots + N_K) \frac{1}{\beta V}$$

$$\bar{p}V = (N_1 + \dots + N_K) kT = (v_1 + \dots + v_K) RT \quad (1)$$

(b) For the i^{th} gas, $p_i V = v_i RT$, hence by (1) $\bar{p} = \sum_i \bar{p}_i$

7.2

(a) By the equipartition theorem the average value of the kinetic energy of a particle is $\bar{E} = \frac{3}{2} kT$.

(b) The average potential energy is $\bar{U} = \frac{\int_0^L mgz e^{-\beta mgz} dz}{\int_0^L e^{-\beta mgz} dz}$

$$\text{Then } \bar{U} = -\frac{\partial}{\partial \beta} \ln \int_0^L e^{-\beta mgz} dz = -\frac{\partial}{\partial \beta} \ln \frac{e^{-\beta mgL} - 1}{-\beta mg}$$

$$\text{On carrying out the differentiation, we find } \bar{U} = kT + \frac{mgL}{1 - e^{-mgL/kT}}$$

7.3

(a) Before the partition is removed, we have on the left, $\rho V = vRT$. After removal the pressure is

$$P_f = \frac{2vRT}{(1+b)V} = \frac{2P}{1+b}$$

(b) The initial and final entropies of the system for different gases are

$$S_i = \nu R \left[\ln \frac{V}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_i \right] + \nu R \left[\ln \frac{bV}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_2 \right]$$

$$S_f = \nu R \left[\ln \frac{(1+b)V}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_i \right] + \nu R \left[\ln \frac{(1+b)V}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_2 \right]$$

Here one adds the entropies of the gases in the left and right compartments for S_i while S_f is the entropy of two different gases in volume $(1+b)V$.

$$\Delta S = S_f - S_i = \nu R \left[2 \ln \frac{(1+b)V}{N_A \nu} - \ln \frac{V}{N_A \nu} - \ln \frac{bV}{N_A \nu} \right] = \nu R \ln \frac{(1+b)^2}{b}$$

(c) In the case of identical gases, S_i is again the sum of the entropies of the left and right compartments. S_f is the entropy of 2ν moles in a volume $(1+b)V$.

$$S_i = \nu R \left[\ln \frac{V}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_o \right] + \nu R \left[\ln \frac{bV}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_o \right]$$

$$S_f = 2\nu R \left[\ln \frac{(1+b)V}{2N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_o \right]$$

$$\text{Thus } \Delta S = \nu R \left[\ln \frac{(1+b)V}{2N_A \nu} - \ln \frac{V}{N_A \nu} - \ln \frac{bV}{N_A \nu} \right] = \nu R \ln \frac{(1+b)^2}{4b}$$

Q.4

(a) The system is isolated so its total energy is constant, and since the energy of an ideal gas depends only on temperature, we have

$$\Delta E_1 + \Delta E_2 = C_V \nu_1 (T_f - T_i) + C_V \nu_2 (T_f - T_2) = 0$$

$$\text{or } T_f = \frac{\nu_1 T_i + \nu_2 T_2}{\nu_1 + \nu_2}$$

The total volume is found from the equation of state

$$V = \frac{\nu_1 R T_i}{P_1} + \frac{\nu_2 R T_2}{P_2}$$

$$\text{Thus the final pressure is } P_f = \frac{(\nu_1 + \nu_2) R T_f}{V} = \frac{\nu_1 T_i + \nu_2 T_2}{(\nu_1 T_i / P_1) + (\nu_2 T_2 / P_2)}$$

(b) Using $\frac{V}{N} = \frac{kT}{P}$, we have for the initial and final entropies of different gases

$$S_i = \nu_1 R \left[\ln \frac{k T_i}{P_1} + \frac{3}{2} \ln T_i + \bar{\sigma}_i \right] + \nu_2 R \left[\ln \frac{k T_2}{P_2} + \ln T_2 + \bar{\sigma}_2 \right]$$

$$S_f = \nu R \left[\ln \frac{k}{\nu_1} \left(\frac{\nu_1 T_i + \nu_2 T_2}{P_1} \right) + \frac{3}{2} \ln \frac{\nu_1 T_i + \nu_2 T_2}{\nu_1 + \nu_2} + \bar{\sigma}_i \right] + \nu_2 R \left[\ln \frac{k}{\nu_2} \left(\frac{\nu_1 T_i + \nu_2 T_2}{P_2} \right) + \frac{3}{2} \ln \frac{\nu_1 T_i + \nu_2 T_2}{\nu_1 + \nu_2} + \bar{\sigma}_2 \right]$$

$$\text{Thus } \Delta S = S_f - S_i = \nu R \left[\ln \left(1 + \frac{\nu_2 T_2 P_1}{\nu_1 T_1 P_2} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{(\nu_1 + \nu_2) T_1} \right] + \nu_2 R \left[\ln \left(1 + \frac{\nu_1 T_1 P_2}{\nu_2 T_2 P_1} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{(\nu_1 + \nu_2) T_2} \right]$$

(C) For identical gases

$$S_i = \nu_1 R \left[\ln \frac{kT_1}{p_1} + \frac{3}{2} \ln T_1 + \sigma_0 \right] + \nu_2 R \left[\ln \frac{kT_2}{p_2} + \frac{3}{2} \ln T_2 + \sigma_0 \right]$$

$$S_f = (\nu_1 + \nu_2) R \left[\ln \frac{k}{\nu_1 + \nu_2} \left(\frac{\nu_1 T_1}{p_1} + \frac{\nu_2 T_2}{p_2} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{\nu_1 + \nu_2} + \sigma_0 \right]$$

$$\Delta S = \nu_1 R \left[\ln \frac{1}{\nu_1 + \nu_2} \left(\nu_1 + \frac{\nu_2 T_2 P_1}{T_1 P_2} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{(\nu_1 + \nu_2) T_1} \right] + \nu_2 R \left[\ln \frac{1}{\nu_1 + \nu_2} \left(\nu_2 + \frac{\nu_1 T_1 P_2}{T_2 P_1} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{(\nu_1 + \nu_2) T_2} \right]$$